Increase in thermal stability induced by organic coatings on nanoparticles

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Based on Lindemann melting criterion and atomic thermal vibration suppression, a thermodynamic model is developed to reveal the mechanism behind the stability of nanoparticles of the smaller size capped with organic molecules. A quantitative description about the increase of the melting temperature of the nanoparticles, due to the interface interaction with organic coatings, is provided by determining the atomic vibrational displacement parameter α. Furthermore, the minimum crystalline nucleus size of the nanoparticles is calculated by combining Turnbull's classical nuclear theory with the size effect of Gibbs free energy.

I. INTRODUCTION

Nanocrystals have drawn a great deal of attention over the past decade due to their peculiar physical and chemical properties compared with the corresponding bulk crystals and the related application potential in electronic, optical and catalytic fields, etc.[1] However, many experiments and theories have shown that the melting temperatures of nanocrystals are much lower than bulk ones.[2] The loss of thermal stability of the nanocrystals will directly affect their synthesis and applications. Aggregation and growth of nanoparticles occur easily due to surface melting and higher surface energy. One important way for preparing nanocrystals is chemical synthesis by a liquid phase method, which forms an organic coating as a passivating layer on the surface of the nanoparticles.[3–8] For example, oleic acid and triphenylphosphine are successfully used to synthesize Co nanoparticles.[8] And organic compounds with thiol molecules are frequently used in synthesizing some noble metallic nanoparticles such as Au, Ag, etc.[3–6] Recently, Pd nanoparticles smaller than 5 nm, capped with *n*-octadecyl mercaptan ($C_{18}H_{37}SH$), have also been synthesized.[7] Applying appropriate surfactants is an effective approach for size control.[3–8] The obtained nanoparticles capped with organic molecules are stable—the interpretation includes the idea that the organic molecules provide larger steric hindrance and the adsorption of thiol on the surface of the nanoparticles decreases the surface energy. However, for nanoparticles with smaller sizes (e.g., smaller than 5 nm), preventing surface melting seems more crucial for the stability of the nanoparticles, since at this size range, the melting point of the nanoparticles decreases acutely, descending even lower than room temperature. This question seems to receive only meager attention.[9] When the surface atomic thermal vibration is suppressed effectively, the melting can be hindered, but how is this realized?

A quantitative understanding of the contribution of organic coatings to the enhancement of thermal stability of the nanoparticles is helpful for sample preparation. In this paper, based on a consideration of atomic thermal vibration, a quantitative model is proposed, to predict the increase of the melting point of the thiol capped nanoparticles compared to that of free-standing nanoparticles, and thus to provide a direct explanation for the mechanism behind the stability enhancement of these nanoparticles. Moreover, the minimum crystalline nucleus size of the nanoparticles is estimated by introducing the size-dependence of related thermodynamic quantities in classical nuclear theory.

II. MODEL AND DISCUSSION

A. Melting temperature

The Lindemann melting criterion, which states that a crystal will melt when the root mean-square displacement (msd) of the atoms in the crystal exceeds a certain fraction of the interatomic distance, is known to be valid for small particles.[10] Let us start from the msd of the atoms of nanocrystals, a quantity related to the melting. The substantial size dependence occurs when the fraction of atoms on the surface becomes significant, so does the msd. Taking the average value with respective weight of the msd of surfacial atoms and that of the interior atoms as the msd over the nanocrystal, a model for the size-dependent amplitude of the atomic thermal vibrations of nanocrystals was proposed.[11] Based on the size-dependent msd of nanocrystals and the relations among the msd, Debye temperature and melting temperature in terms of the Lindemann criterion with the Debye model,[11] an expression for the size-dependent melting temperature function $T_m(D)$ of nanocrystals was developed,[11–13]

$$\frac{T_m(D)}{T_m(\infty)} = \frac{\sigma^2(\infty)}{\sigma^2(D)} = \exp\left[\frac{-(\alpha-1)}{D/D_0 - 1}\right], \quad (1)$$

where $T_m(\infty)$ is the corresponding bulk value of $T_m(D)$. $\sigma^2(D)$ and $\sigma^2(\infty)$ are the averaged msd of atoms for a crystal with a diameter of D and for the corresponding bulk crystal, respectively. Equation (1) is consistent with experimental findings.[11–13] D_0 in Eq. (1) is defined as a critical diameter at which almost all atoms are at the crystal's surface. Let h be the atomic or molecular diameter, D_0 of a spherical nanoparticle is given by[11–13]

$$D_0 = 6h. \quad (2)$$

In Eq. (1), α is a ratio of msd of surface atoms of the nanocrystals $[\sigma_s^2(D)]$ to that of atoms within the nanocrystals

$[\sigma_v^2(D)]$,[11–13] $\alpha = \sigma_s^2(D)/\sigma_v^2(D)$. Note that the two basic assumptions in the model of the size-dependent atomic thermal vibrations of nanocrystals are (1) although $\sigma_s^2(D)$ and $\sigma_v^2(D)$ of nanoparticles are considered to be size-dependent (the phonon softening is considered to occur not only on the surface but also in the interior for the small size crystals from a microscopic concept), the ratio between them α is taken approximately as a size independent value; (2) the cooperative coupling between the surface region and the interior region is considered phenomenologically by taking the variation of the msd averaged over the nanocrystal to be dependent on the value of $\sigma^2(D)$ itself.[11] With the above consideration, a change in σ can be given by $\sigma^2(x+dx) - \sigma^2(x) = (\alpha-1)\sigma^2(x)dx$, where x is the surface/volume ratio $D_0/(D-D_0)$.[11] By integration of the above equation, the size-dependent msd was obtained as shown in Eq. (1). From the point of view of the bulk approach, there are two asymptotic limits to be satisfied by Eq. (1): $D \to D_0$, $\sigma^2(D)/\sigma^2(\infty) \to \infty$, $T_m(D)/T_m(\infty) \to 0$; $D \to \infty$, $\sigma^2(D)/\sigma^2(\infty) \to 1$, $T_m(D)/T_m(\infty) \to 1$. The critical size of order D_0 represents a length scale characteristic for the crystallinity. The model has been proved to be valid to predict the melting of nanocrystals with the size $D > D_0$ (Refs. 11 and 12) and is inapplicable when D decreases to D_0, since Eq. (1) loses its meaning at $D=D_0$. For the particles with the size $D < D_0$, the small size effect and large surface/volume ratio of nanoparticles may not be sensible, the quantized phonon characteristic or oscillational size effect may be dominant for particles with such a small size.[14]

According to Eq. (1), if the parameter α is determined, the thermal stability of nanoparticles with the size D can be known. For the general case, when the surface of the nanocrystals is fully free, $\sigma_s^2(D) > \sigma_v^2(D)$ and $\alpha > 1$, according to Eq. (1), $T_m(D) < T_m(\infty)$, i.e., the melting point decreases, where α takes its largest value,[12]

$$\alpha_{max} = 2S_m(\infty)/(3R) + 1, \qquad (3)$$

where $S_m(\infty)$ is the melting entropy of the corresponding bulk crystals and R is the ideal gas constant. On the other hand, when the surface of a nanocrystal is confined enough, $\sigma_s^2(D) < \sigma_v^2(D)$ and $\alpha < 1$, $T_m(D) > T_m(\infty)$, this is the case of superheating for some special confined systems.[13]

For the thiol capped metallic nanoparticles, the atomic vibration on the interface is different from that on the free surface. Since the thiol molecules interact with the surface atoms of the nanoparticles, the surface atomic vibration is suppressed and the msd decreases. If the msd of the surface atoms interacting with S atoms of the thiol molecules is assumed to be the same as that of the atoms within the nanoparticles, according to the definition of α, we have $\alpha = [(1-\beta)\sigma_s^2(r) + \beta\sigma_v^2(r)]/\sigma_v^2(r)$, where β denotes a ratio of the number of surface atoms interacting with S atoms to the total surface atomic number. This assumption is reasonable since the binding energy between the metallic atoms and S atoms is comparable with the cohesive energy of the metallic atoms—for example, binding energy 127.9 Kcal mol^{-1} of Pd and S (Ref. 15) is even higher than cohesive energy 89.8 Kcal mol^{-1} of Pd.[16] Comparing with Eq. (3),

$$\alpha = \alpha_{max}(1 - \beta) + \beta, \qquad (4)$$

with $\beta = n/N$, where $N = (D/h)^3(D_0/D)$ shows the total surface atomic number of the nanoparticles, $n = \pi D^2/s$ denotes the number of the surface atoms interacting with the S atoms—i.e., the number of thiol molecules capping the surface of the nanoparticles—s is the area occupied by one thiol molecule. Note that the number of thiol molecules is enough to cap the whole surface of the nanoparticles considering the general molar ratio in the experiments.[3–8] Substituting Eq. (3) into Eq. (4), and then substituting Eqs. (2) and (4) into Eq. (1), the melting temperature of the thiol capped nanoparticles can be predicted.

Equation (1) shows α and D dependencies of the melting temperature of nanoparticles—$T_m(D)$ increases with decreasing α, and when $\alpha > 1$, $T_m(D)$ decreases with decreasing D, vice versa. Because of the interaction between the surface atoms of the nanoparticles and the organic coating molecules and thus the suppression of the surface atomic vibration, α in Eq. (4) is smaller than that determined by Eq. (3), and thus the melting point of the nanoparticles capped with organic molecules is enhanced compared with that of the free-standing nanoparticles expressed by Eqs. (1) and (3), although α is still larger than 1.

Note that the validity of Eq. (4) depends on the stability of the organic coatings—if they melt and diffuse, the nanoparticles will be uncapped and melt at a lower temperature. Therefore, the melting temperature of the organic coatings should be considered. For the organic coating crystals, the melting temperature is enhanced, more or less, compared to that of the corresponding bulk organic crystals, due to the interaction between the organic molecules and the surface atoms of the metallic nanoparticles and the higher melting point of metals. Suppression of surface molecular vibration is considered for the organic coatings, whose melting temperature is also expressed by Eq. (1). The difference is that the parameters in the equation in that case are of course related to the organic coatings—not to the metallic particles as in the above discussion—and α is smaller than 1. Considering the stronger binding between Pd and S atoms and thus greater suppression of molecular vibration, α in Eq. (1) is assumed to take its smallest value,[13]

$$\alpha_{min} = [(h_M/h_O)^2 T_O(\infty)/T_M(\infty) + 1]/2, \qquad (5)$$

where h_M and h_O denote the metallic atomic diameter and the organic molecular diameter, respectively. $T_M(\infty)$ and $T_O(\infty)$ are the bulk melting points of the metallic particles and the organic coatings, respectively. Because $h_M < h_O$ and $T_O(\infty) < T_M(\infty)$, according to Eq. (5), $\alpha < 1$, the melting point of the organic coatings increases. Combining Eqs. (5) with (1), the melting temperature function $T_O(D)$ of the organic coatings can be obtained, and $T_O(D) > T_O(\infty)$. Note that $D_0 = 4h_O$ in Eq. (1) is taken for the organic coatings as a first order approximation, since D_0 is equal to $6h$ for spherical particles and $2h$ for thin films[12] and the dimension of the organic coatings with the spherical shell shape is between the dimension of the particles and that of the films.

It can be seen from Fig. 1 that when the size of Pd nanoparticles is smaller than 3 nm, the melting point of free-
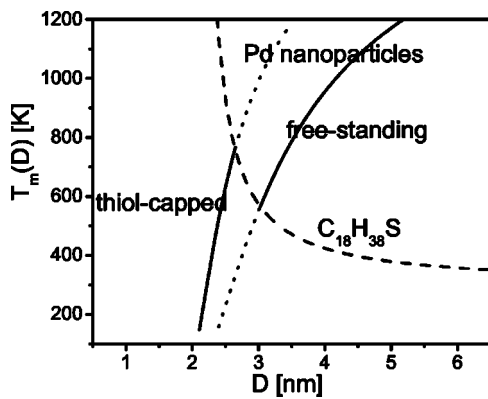
FIG. 1. The melting temperature $T_m(D)$ of Pd nanoparticles in terms of Eq. (1) shown as solid lines. The dotted lines are the extended lines to aid the eyes. The dashed line shows the melting temperature $T_O(D)$ of $C_{18}H_{38}S$. For Pd, $h=0.304$ nm (Ref. 17), $D_0=6h=1.824$ nm in terms of Eq. (2). And $T_m(\infty)=1825$ K (Ref. 18) in Eq. (1). While $H_m(\infty)=17.6$ kJ mol^{-1} (Ref. 18), and $S_m(\infty)=H_m(\infty)/T_m(\infty)=9.644$ J mol^{-1} K^{-1}, $\alpha_{max}=1.773$ in terms of Eq. (3) for the free-standing Pd nanoparticles. For $C_{18}H_{38}S$, the molar volume $V_O=M/\rho=338.124$ cm^3 mol^{-1} with molecule mass $M=286.56$ g and density $\rho=0.8475$ g cm^{-3} (Ref. 19), while $h_O=[V_O/(n_O N_a)]^{1/3}=338.124$ cm^3 mol$^{-1}/(18N_a)=0.315$ nm with the number of segments per molecule $n_O=18$ and Avogadro constant N_a. Therefore, $s=h_O^2=0.099$ nm^2, $\beta=n/N$ $=(\pi D^2)/s/(D^3/h^3)(D_0/D)=\pi h^3/(sD_0)=0.49$, $\alpha=1.394$ in terms of Eq. (4) for Pd nanoparticles capped with $C_{18}H_{38}S$. $T_O(\infty)$ $=297.15$ K (Ref. 19), $\alpha_{min}=0.576$ in terms of Eq. (5) for $C_{18}H_{38}S$.

standing nanoparticles decreases dramatically and falls even below room temperature. But it increases several hundred degrees for the nanoparticles with thiol capping. For example, for the Pd particle of 2.6 nm, the melting point is enhanced from 300 K to 730 K as shown in Fig. 1. When D is larger than 3 nm, the melting temperature of the organic coating $C_{18}H_{38}S$ is lower than that of free-standing Pd nanoparticles, and its effect on enhancing the melting point of the nanoparticles will disappear. On the other hand, Eq. (1) is inapplicable when D decreases to D_0—i.e., the melting temperature cannot reach 0 K, and $D_0=1.824$ nm for Pd. Moreover, the structure and energy states for particles with such a small size may be special, as will be discussed in detail later, and their stable temperature may relatively increase.

Similarly, the melting point of Au nanoparticles with a size smaller than 3 nm capped with $C_{12}H_{25}SH$ also increases about 400 K from under 273 K, based on our model's calculation. Otherwise, Au and Pd nanoparticles smaller than 3 nm cannot be obtained at room temperature, which would conflict with the results of experimental synthesis.[3,7] On the other hand, the temperature increase of 400 K reflects a potential energy depression of about 0.04 eV for the system. Therefore, the interaction between the organic molecules and the surface metallic atoms indeed increases thermal stability of the smaller sized metallic nanoparticles. This stability is significant not only for synthesizing nanoparticles but also for constructing superlattice.

B. Gibbs free energy

Equation (1) predicts the size-dependent melting point $T_m(D)$ of nanocrystals. The size-dependent melting entropy $S_m(D)$ based on Mott's model for the vibrational entropy of melting is expressed as[12]

$$S_m(D) = S_m(\infty) - (3R/2)(\alpha - 1)/(D/D_0 - 1), \quad (6)$$

where $S_m(\infty)=H_m(\infty)/T_m(\infty)$ with the bulk melting enthalpy $H_m(\infty)$. Combining Eqs. (1) and (6), the size-dependent melting enthalpy $H_m(D)=T_m(D)S_m(D)$ and thus

$$H_m(D) = H_m(\infty)\exp\left[\frac{-(\alpha-1)}{D/D_0-1}\right]\left[1 - \frac{3R}{2S_m(\infty)}\frac{\alpha-1}{D/D_0-1}\right]. \quad (7)$$

Similarly, although the melting enthalpy and entropy decrease dramatically as the size of free-standing nanoparticles decreases, this decline is much compensated by the organic coatings. Substituting Eq. (3) and (4) into Eq. (6), respectively, and then comparing the two resulting equations with each other, the increase or the compensation of the entropy can be calculated, and substituting Eqs. (3) and (4) into Eq. (7), the same can be accomplished for enthalpy. According to the calculation, the melting enthalpy increases several kilojoules due to capping, in agreement with the above discussion of potential depression.

It is well known that for the crystallization phase transition, the volume Gibbs free energy difference g between the crystal and the corresponding liquid, as a function of the temperature T, is expressed as[20]

$$g = H_m(D) - TS_m(D). \quad (8)$$

Note that the thermodynamic equilibrium phase transition is discussed here, and thus the crystallization enthalpy and entropy are equal to the melting enthalpy $H_m(D)$ and entropy $S_m(D)$, respectively. The only difference from the classic expression is the introduction of the size effect of the related quantities. According to Turnbull's nuclear theory,[21] the total Gibbs free energy change G of the system during the nucleation process includes the volume energy term and the surface or interface energy term like this,

$$G = -(g/V_s)\pi D^3/6 + \pi D^2\gamma, \quad (9)$$

where V_s is the molar volume of the crystal, and γ is the solid-liquid interface energy. Substituting Eqs. (6) and (7) into Eq. (8), and then substituting Eq. (8) into Eq. (9), G can be obtained. We adopt the subscript $i=1, 2$ to consider G_i for the two cases of the free-standing and organic molecules capped nanoparticles, respectively. It is clear that the difference between G_1 and G_2 results from the differences between g_1 and g_2, γ_1 and γ_2. The difference between g_1 and g_2 is finally determined by Eqs. (3) and (4). The equality $\gamma_2=\gamma_1/2$ is assumed here considering the decrease, of about one-half, of surface dangling bonds, with $\beta \approx 1/2$ due to the interaction between the organic molecules and the surface metallic atoms.

As it is known, the maximum of G corresponds to the minimum critical crystalline nucleus size and crystallization occurs spontaneously when $G < 0$.[21] It can be seen from Fig. 2 that the crystalline nucleus size of the thiol capped Pd nanoparticles (see G_2) is smaller than that of the free-standing nanoparticles (see G_1), about 2.5 nm and 3.3 nm,
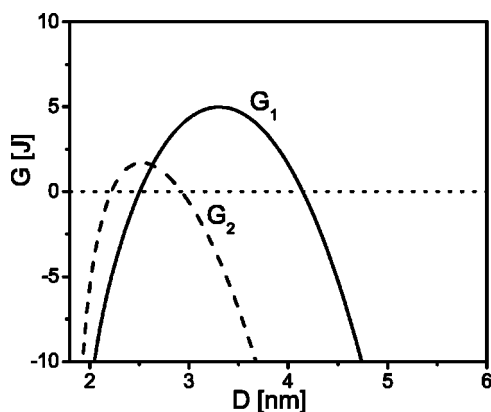
FIG. 2. The total Gibbs free energy change as a function of the grain size of Pd in terms of Eq. (9). G_1 and G_2 are shown as the solid line and the dashed line, respectively. The dotted line corresponds to $G=0$. $V_s=8.9$ cm^3 mol^{-1} (Ref. 18). $\gamma_1=\gamma_1(\infty)(1-D_0/D)$ (Ref. 22) with the bulk value $\gamma_1(\infty)=0.2$ J m^{-2} (Ref. 23). The size effect of solid-liquid interface energy is considered here.

respectively. The result indicates that the thiol capped nanoparticles can obtain a smaller grain than the free-standing nanoparticles can. Note that the above equations are inapplicable when D decreases to D_0. When $D \rightarrow D_0$, the nanoparticles will not be crystals strictly speaking, but more exactly clusters. The structures of clusters are different from those of the corresponding crystals-clusters tend to have the lower energy configuration[24] and thus greater stability. Therefore, even smaller particles can be produced.

The above theoretical prediction and analysis agrees with the recent experimental synthesis of 1.3–5.5 nm Pd nanoparticles.[7] On the other hand, this agreement from the thermodynamic point of view implies the existence of the chemisorption between the nanoparticles and capping mol-

ecules, since the stronger chemical binding contribution are included in G_2 by α, H_m, S_m, g, and γ corresponding to Eqs. (4) and (6)–(9). Note that the discussion here is related with the thermodynamic equilibrium state as a premise, and the details of the experimental circumstances and other dynamic factors also have important influence. A further study of the competition among nucleation, adsorption, and growth rates may provide a clearer scenario for the formation of smaller nanoparticles or nanoclusters.

III. CONCLUSION

In summary, the thermal stability of nanoparticles capped with organic molecules was first quantitatively analyzed by introducing a thermodynamic melting model and developing the atomic vibration parameter α. The result indicates the suppression of the surface atomic vibration, resulting from the interaction with organic capping molecules, enhances the melting temperature and thus the stability of the nanoparticles. Furthermore, the achievement of the smaller grain was explained on the basis of classic nuclear theory by introducing the size effect of related parameters. In conclusion, the role of organic molecules is important to the stability of nanoparticles. Apart from providing steric resistance, these organic molecules also decrease the system energy and effectively prevent the melting of small size nanoparticles.

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